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Paper

A Synchrotron Radiation Photoelectron Spectroscopic Study on the Oxidation of Si in Diamond-like Carbon Film by Hyperthermal O-atom Beam

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Oxidation reaction efficiency of the embedded Si atoms in the diamond-like carbon (DLC) film was studied with a combination of the broad O-atom beam, high-speed chopper wheel and synchrotron radiation photoelectron spectroscopy (SR-PES). The high-speed chopper wheel converted the translational energy distribution of O-atom into spatial distribution on the DLC surface. High spatial and energy resolutions of SR-PES allow studying the difference in oxidation states of Si atoms in different translational energies. It was confirmed that the SiO_2 was formed by the high-energy collision conditions of O-atoms, whereas sub-oxides are formed with the low-energy collisions. The efficiency of SiO_2 formation at 9 eV-collision is evaluated to be 4 times greater than that at 2 eV-collision.

1. Introduction

There exist many environmental factors in low Earth orbit (LEO) such as micro-gravity, thermal cycling, plasma, ultraviolet, radiation, neutral gas and space debris. In particular, one of the most important factors that gave serious damage to the many polymeric materials is O-atom which is a dominant neutral species in LEO. Due to its high chemical reactivity and high impact energy, O-atom in LEO erodes many materials used in the exterior surface of spacecraft especially carbon-based materials such as polymers and diamond-like carbons (DLCs) [1-3].

Embedded Si atoms in the main chain of polymer is a promising technology to protect polymeric materials from a harsh space environment in LEO. When Si atoms in the main chain of polymers are oxidized by O-atom bombardment in LEO with collision velocity of 8 km/s (collision energy of 5 eV), it is expected that the non-volatile SiO_2 layer was formed at the surface. The formation of SiO_2 layer at the polymer surface in LEO provides the capability of self-healing protective materials against O-atom attack in LEO [4]. Therefore, understanding of the oxidation reaction of O-atom with Si with collision energies in a few electron volts is important for space engineering.

On the other hand, the oxidation of Si at low temperatures is also crucial as a semiconductor fabrication technology. Many of such low temperature processes use oxygen plasma which includes O-atoms as an oxidant. However, the oxidation reaction of Si by O-atom has not been fully understood through experiments. One of the reasons is the difficulty of creating a high-density O-atom environment without any byproduct. Namely, oxygen plasma usually involves not only O-atoms, but also excited O_2 molecules and ions. The presence of such chemically reactive byproducts makes the analysis of the reactivity of O-atoms difficult. Therefore, a high-purity O-atom environment is necessary to study the oxidation reaction of O-atoms with Si.

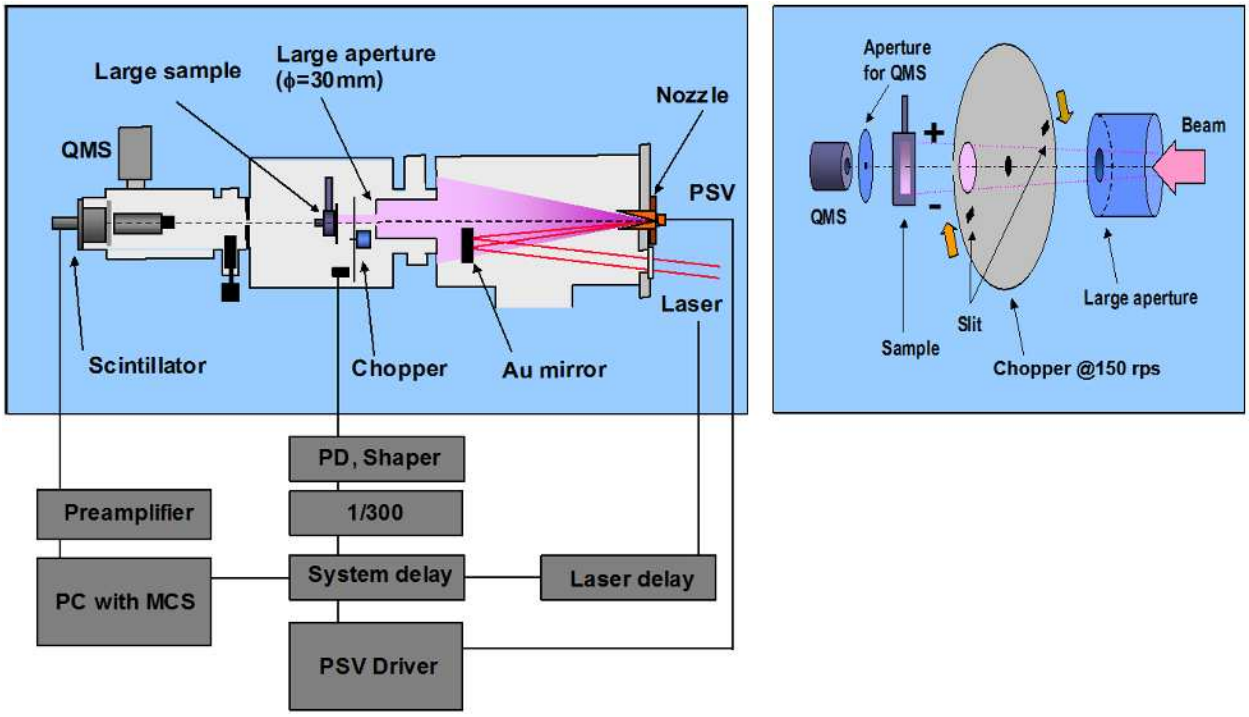

Fig. 1 The system diagram and detail of the velocity– position conversion by the chopper wheel. The O-atom beam with diameter of 30 mm was sliced by the chopper wheel rotating 150 rps (two slits on the disc). A photodiode signal (300 Hz) was reduced to 1 Hz and used as a system clock. Because of the CW rotation of the wheel, the negative positions on the surface are high-energy exposure positions.

In this study, energy dependence in oxidation reaction of Si atoms in DLC films was studied by the hyperthermal O-atom beam condition which simulates space environment in LEO. It has been known that the O-atom beam produced in this method contains small amount of undecomposed O_2 and almost no ion [5, 6]. It is much more pure O-atom environment than in O_2 plasma. Thus, the data obtained in this study would be useful for understanding of the oxidation reactions in O-atom and Si system.

2. Experimental Details

The hyperthermal O-atom beam was produced by the laser-detonation facility which has been used for simulating high-energy (5 eV) collision phenomena of O-atom with materials in LEO (Fig. 1). The detail of the facility was reported elsewhere [6]. A combination of the broad O-atom beam generated by the laser-detonation method and the high-speed mechanical chopper wheel (150 rps) was applied in this study. This combination could convert a velocity distribution of the O-atom beam into a spatial distribution on the specimen surface. The time-of-flight (TOF) distributions at the sample position from –6 to +12 mm from the beam axis are shown in Fig. 2. Position "±0" represents the center position of the sample (on the beam axis). The TOF distributions at the out-of-axis positions were measured by the on-axis QMS at the same slicing timing. Difference in spatial distribution on the TOF distributions was ignored since the 12 mm on the sample surface corresponds to less than 1° in the viewing angle from the nozzle throat. It was analyzed from these TOF spectra that the collision energy of O-atom distributed from 2 to 9 eV depending on the location of the specimen. The flux variation with energy in the sliced beam was compensated by the intensity of TOF distribution of the sliced beam. Figure 3 shows the energy and intensity distributions over the sample surface. It was confirmed that the maximum flux was obtained at the location of +4 mm position, where the average O-atom energy is 2.5 eV. The negative positions are exposed to the O-atom beam with low-flux but high-energy. The Si-DLC sample (15 mm x 30 mm) was cleaved from a DLC-coated Si wafer which was prepared by CVD method. The DLC layer

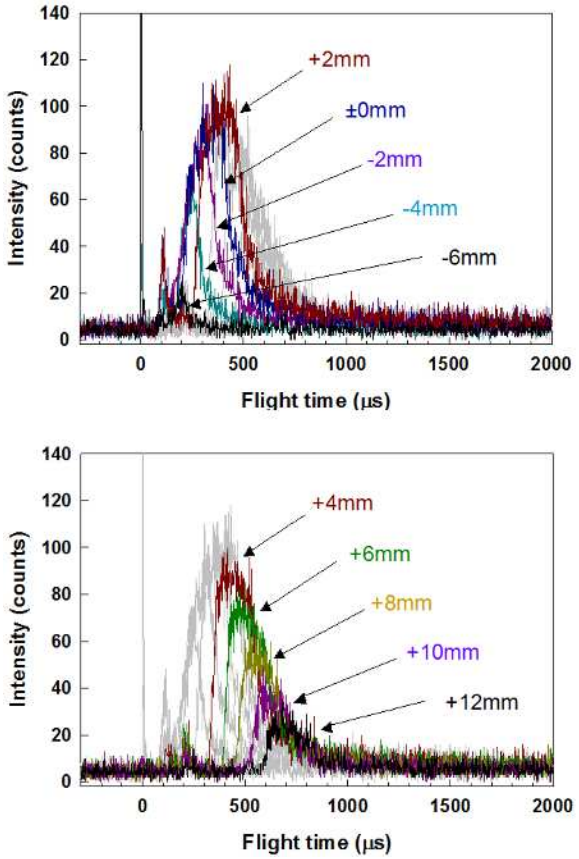

Fig. 2 Sliced TOF distributions of O-atom at the sample positions relative to the center axis of the apparatus. The TOF spectra of the O-atom at high-energy positions on the sample are shown in the top panel. Those at low-energy positions are shown in the bottom panel. The time zero in the abscissa represents the moment of laser fires.

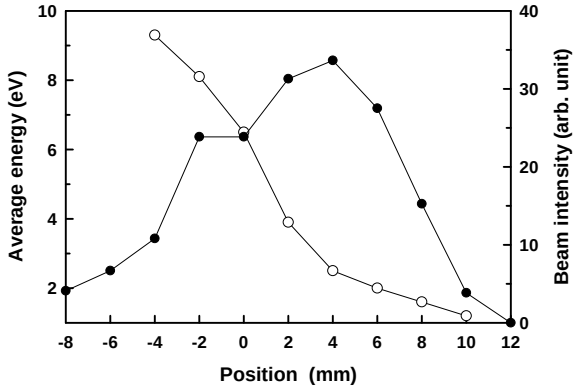

Fig. 3 Average energy and flux distributions over the sample surface. ○: Average energy and ●: Beam intensity

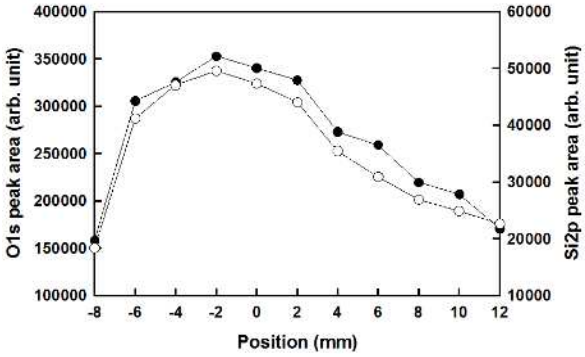

Fig. 4 Comparison of Si2p and O1s SR-PES signal intensities on the sample surface. ○: Si2p and ●: O1s

was 1 μm in thickness and Si content was approximately 10 at%. The hydrogen content of the sample estimated by the elastic recoil detection analysis (ERDA) is roughly 30 at%, respectively.

The synchrotron radiation photoelectron spectroscopy (SR-PES) measurements were performed by the SUREAC2000 end-station at the BL23SU in the SPring-8 facility. The SR-PES measurements were carried out with X-ray energy of 849.7 eV. All SR-PES spectra were taken with the take-off angle of 90° (surface normal).

3. Results and Discussion

Figure 4 shows the SR-PES O1s and Si2p intensity distributions over the sample surface. O1s intensity shows the summit between –6 and +2 mm where relatively low-flux and high-energy positions. This result clearly indicated that the accommodation coefficient of O-atom at Si-DLC surface has strong energy dependence. The Si2p signal intensity distribution also shows the similar distribution with O1s which suggests the O-atom is chemically bonded with Si atoms and remains at DLC surface. This result was supported by the fact that the C atoms in DLC was removed by forming volatile products such as CO and CO_2 [7].

Figure 5 shows the SR-PES Si2p core level of the Si-doped DLC at different positions normalized by the peak intensity at 100.8 eV. The relative intensity of the peak at 103.7 eV depends on the position on the sample surface. The chemical shifts of Si2p with respect to metallic Si was reported as follows; Si_2O (+1.0 eV), SiC (+1.1 eV), SiO (+2.0 eV), Si_2O_3(+3.0 eV) and SiO_2 (+4.0 eV) [8]. The chemical shift of 2.9 eV shown in Fig. 5 reflects the conversion from SiC structure to SiO_2

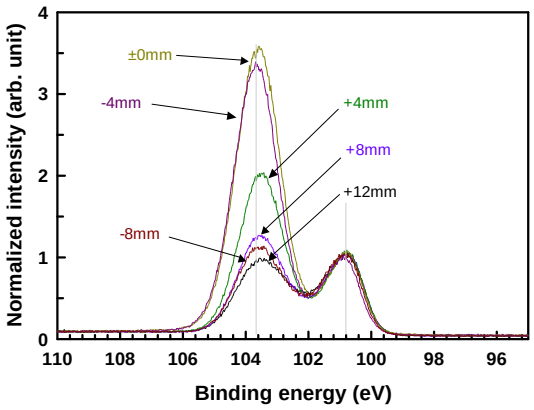

Fig. 5 Change in Si2p SR-PES spectra measured at the sample surfaces from –8 to +12 mm positions.

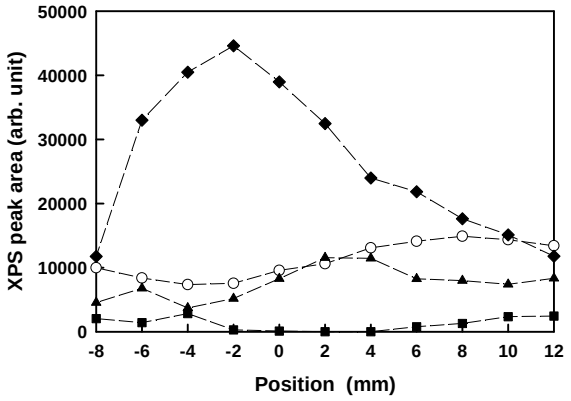

Fig. 6 Peak deconvolution results of Si2p SR-PES spectra over the O-atom beam-exposed sample surface. ○: SiC, ■: SiO, ▲: Si_2O_3, ◆: SiO_2.

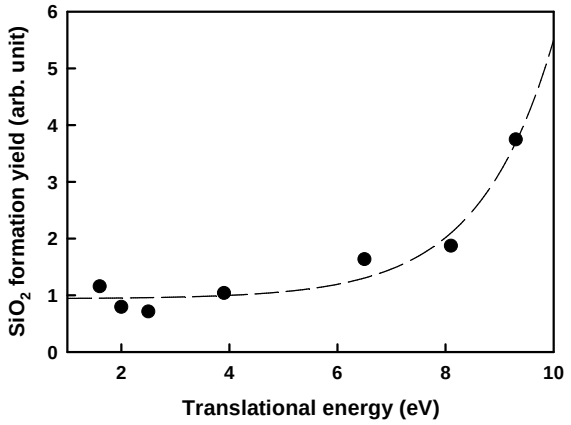

Fig. 7 Translational energy dependence on the reaction yield of O-atom with Si in DLC. The dashed line is the regression result.

structure by O-atom reaction. This result was supported by the fact that the native oxide of SiC is SiO_2. The Si2p peaks were deconvoluted by 5 sub-peaks consisting of SiC, SiO_x (x = 0, 1, 1.5 and 2). The results of deconvolution are shown in Fig. 6. It was clearly indicated that the SiO_2 intensity has a summit at the –2 mm position which is low-flux but high-energy O-atom-exposed region. In contrast, sub-oxide (Si_2O_3) is distributed at the +4 mm position where low-energy O-atoms reacted. It was also observed that the peak intensity of suboxides decreased with increasing the collision energy of incoming O-atom. The peak intensity of SiO_2 is rapidly increased at the position of +4 mm which corresponds to the translational energy of 2.5 eV even though the flux decreased (see Fig.3). It was thus concluded that the formation of SiO_2 by the O-atom collision is promoted by the translational energy higher than 2.5 eV at room temperature.

The reaction yield of O-atom with Si-atom in DLC was evaluated by the SR-PES SiO_2 signal divided by O-atom flux. The results are shown in Fig. 7. It is clearly indicated that the reaction yield of O-atom increased exponentially with increasing translational energy. The reaction yield at 9 eV is 4 times greater than that at 2 eV. The Si-atoms in DLC are considered to bond with neighboring C atoms, which form Si-C bonding. Oxidation of Si-C bonding has been studied relating to the SiC-based devices. However, a limited number of publications are available for SiC oxidation by O/O_2 beam. Takahashi et al studied the initial oxidation reaction of 4H-SiC(0001) with 0.5 eV O_2 beam. They reported that the O_2 molecule is immediately dissociated at the SiC(0001) surface and O-atoms are inserted into Si-Si backbond to form stable oxide [9]. The translational energy dependence on the O/O_2 reactions with SiC has not been reported to date. The result of this work suggests that the SiO_2 formation on the Si atoms in DLC is promoted by the O-atom translational energy greater than 5 eV which is the collision environment in LEO. Moreover, N_2 molecule in LEO simultaneously collides to DLC at 9 eV because of its larger mass. The simultaneous collision of 5 eV O-atom and 9 eV N_2 could accelerate the oxidation of Si-atom at DLC surface if N_2 collision provides the energy to overcome the potential barrier of the oxidation reaction (collision-induced oxidation). The presence of this synergistic effect is still to be discovered.

4. Conclusions

The translational energy dependence on the oxidation efficiency of Si atom in DLC was studied with hyperthermal O-atom beams. It was confirmed that the oxidation yield of O-atom with Si increase exponentially with the collision energy of O-atom in the range of 2 to 9 eV. It was also examined that the amount of suboxides decreased with increasing the collision energy of incoming O-atom above 4 eV. It was concluded that formation of SiO_2 by the collision of energetic O-atom in LEO is promoted with the orbital velocity of spacecraft at 8 km/s, which corresponds to the collision energy of 5 eV.

5. Acknowledgments

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6. References

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